PPh_3, but the slower carbon epimerization rates are.

On the basis of the preceding observations, we propose that rhenium and carbon epimerization proceed via the key steps shown in Scheme I. The trigonal-planar intermediate **3** partitions between a return to **2** (accelerated by added PPh_3) and a slower β-hydride elimination to give the ketone complex **4**. Exchange of R and R′ in the ketone complex—a process known to be extremely facile in either σ or π coordination modes[9]—and reversal of the hydride elimination completes the carbon epimerization process. There is abundant precedent for the β-hydride elimination in alkoxide complexes,[10] although in most cases concomitant extrusion of a ketone or aldehyde appears to occur.[4] Finally, rate experiments with pentamethylcyclopentadienyl complexes establish a *much* faster PPh_3 dissociation, but apparently only slightly faster β-hydride elimination.

In summary, we have discovered a convenient and unusual new alcohol epimerization catalyst, the chirality of which allows a detailed probe of mechanism. Additional data pertaining to the nature of the reaction coordinates of these carbon–hydrogen bond activation processes will be described in our full paper.

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Supplementary Material Available: Listings of characterization data for complexes **1**-Me_5 and **2a** (7 pages). Ordering information is given on any current masthead page.

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[9] (a) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198. (b) Quirós Méndez, N.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475.

[10] For particularly relevant examples, see: Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531 and references therein.

Activation of Organomagnesium Reagents by Crown Ethers: Unusual Ether Cleavage of (2-Methoxy-1,3-xylylene)-15-crown-4

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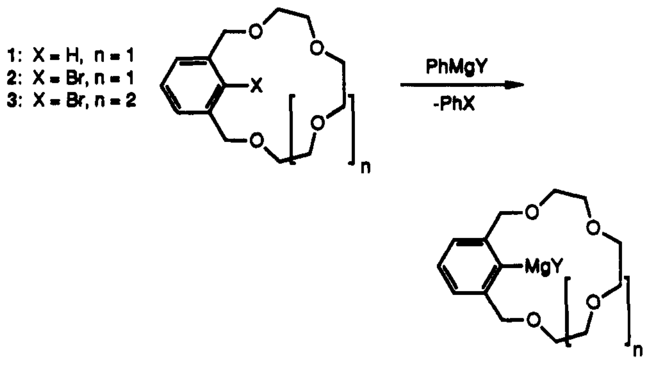
Summary: The reaction of (2-methoxy-1,3-xylylene)-15-crown-4 (**4a**) with diphenylmagnesium *at room temperature* resulted in the cleavage of the methyl–oxygen bond with unprecedented ease, leading to (2-hydroxy-1,3-xylylene)-15-crown-4 (**10**) and toluene. In order to rationalize this unusually high reactivity, we suggest a transition state (**8** or **9**) with both an electrophilic and a nucleophilic component: the cationic magnesium atom is involved in an electrophilic attack on the oxygen, while the magnesate counterion attacks the methyl group in an S_N2 process.

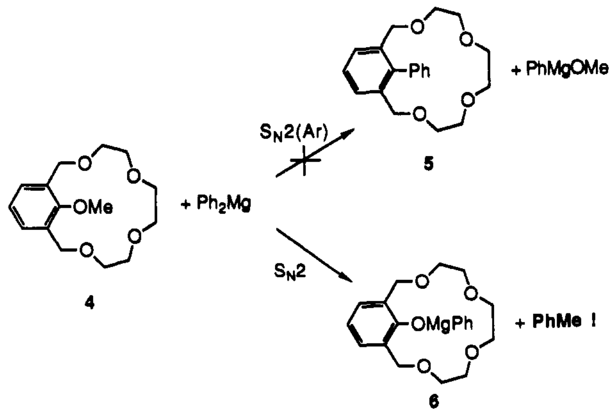
Crown ethers may exert a profound influence on organomagnesium reagents; unusual structures as well as unusual reactivities have been encountered.[1,2] In the present context, the strongly enhanced reactivity of diphenylmagnesium, and to a lesser extent that of phenylmagnesium bromide, toward (derivatives of) (1,3-xylylene)-15-crown-4 and (1,3-xylylene)-18-crown-5 is of relevance: metalation or halogen–metal exchange occurs, which is uncommon for organomagnesium compounds but reminiscent of the behavior of organolithium compounds (Scheme I).[1a,c]

Scheme I[a]



[a] Y = Ph, Br.

Scheme II



This unusual reactivity was tentatively explained[1c] by specific coordination of the organomagnesium species to the crown ether. As a result, the polarization of the

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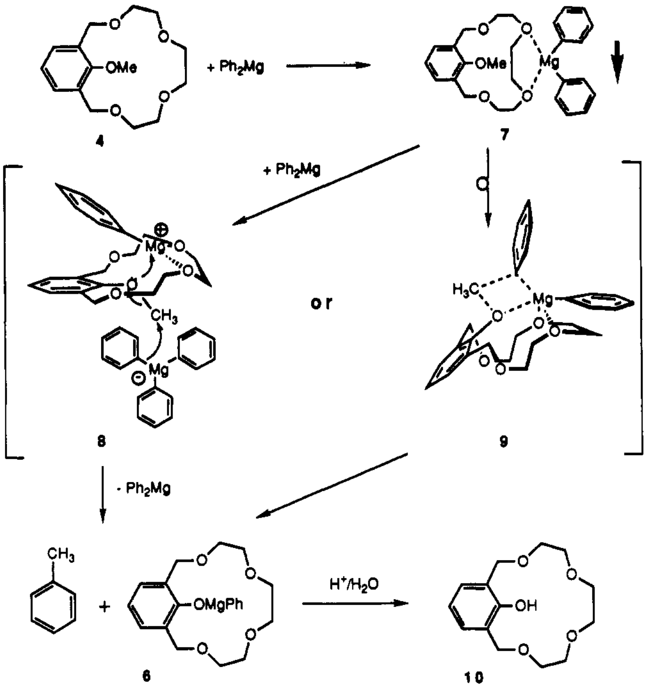
[1] (a) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Angew. Chem.* **1988**, *100*, 1143. (b) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4845. (c) Markies, P. R. Thesis, Vrije Universiteit, 1990. (d) A similar "side-on" structure was tentatively identified for **1**[1a] and for the rotaxane from (1,3-xylylene)-18-crown-5 and diphenylmagnesium[1b] by ^1H NMR spectroscopy; for the combination of **2** and **3** with the less reactive diphenylzinc, X-ray crystal structures confirm this assignment.[1c,e] (e) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L., submitted for publication.

[2] (a) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. (b) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

Scheme III



magnesium–phenyl bond is increased, which facilitates electrophilic attack of magnesium on the ipso carbon while, simultaneously, the phenyl anion (or rather its magnesate equivalent) attacks the atom X (H or Br, respectively), leading to cleavage of the C–X bond.

It was desirable to obtain further support for this proposal. Therefore, the behavior of (2-methoxy-1,3-xylylene)-15-crown-4 (**4a**) toward organomagnesium compounds was investigated. This choice was based on the following considerations. In the first place, an anisyl ether function is notoriously inert against organometallics; if a reaction did occur, it would demonstrate extraordinary reactivity indeed. Second, **4a**, unlike **1**–**3**, is not expected to undergo nucleophilic attack by the phenyl "anion" at the atom directly bonded to the ipso carbon, which in this case is oxygen. Instead, electrophilic attack of magnesium on this oxygen might go along with two different modes of cleavage: that of the oxygen–aryl bond ($S_N2(Ar)$ at the ipso carbon), leading to **5**, or of the oxygen–methyl bond (S_N2 at the methyl carbon), leading to **6** (Scheme II). It is the latter reaction which was actually observed.

When **4a**[3a] was added to a solution of 1 molar equiv of diphenylmagnesium in diethyl ether solution, a white precipitate formed almost instantaneously; presumably, it contained the "side-on" complex **7** (Scheme III).[1d] Immediate quenching of this reaction mixture with dilute hydrochloric acid showed the formation of 2% of **10** (^{1}H NMR) and 2% of toluene (GCMS); 98% of unreacted **4a** could be recovered. In other experiments, after 1 h at room temperature, the supernatant was separated from the solid by decantation and analyzed by GC. In this supernatant, up to 50% toluene was detected by gas chromatography; however, in an experiment performed in [D_{10}]diethyl ether in a system sealed under high vacuum, ^{1}H NMR spectroscopy indicated practically quantitative formation of toluene. The solid residue was hydrolyzed with dilute hydrochloric acid and gave the phenolic crown ether **10**[3b] (^{1}H NMR) in >95% yield and benzene (GC). Similarly, reaction of **4a** with bis(*p*-*tert*-butylphenyl)magnesium gave, after hydrolysis, *p*-*tert*-butyltoluene and **10** (90%). With phenylmagnesium bromide, **4a** reacted correspondingly to furnish toluene and (presumably) the bromomagnesium salt of **10** (analogous to **6**), but the reaction was much slower: at 50 °C, the conversion of **4a** was 59% after 1 day and (in another experiment) complete after 2 days.

The S_N2 attack of a (formal) phenyl anion on an aliphatic carbon with a phenoxide anion as a relatively poor leaving group is, to our knowledge, without precedent; it comes down to the alkylation of an organomagnesium by an anisole!

A $S_{RN}1$ mechanism,[4] initiated by a single-electron transfer (SET; eq 1), is unlikely for several reasons which will be discussed in a full paper. Most convincingly,

$$7 + 4 \rightarrow Ph^{\bullet} + [PhMg^{\bullet+}4] + 4^{\bullet-} \qquad (1)$$

however, $S_{RN}1$ is excluded by the observation that the ethyl analogue of **4a** (**4b**) reacted very slowly (36 h at 45 °C; 11% conversion) to give **6** and ethylbenzene, while the isopropyl analogue **4c** gave no reaction at all (72 h at 45 °C). If a SET mechanism were operating, the reaction should not depend dramatically on the nature of the alkyl substituent (and if so, probably in the opposite direction), whereas the observed reactivity order **4a** > **4b** >> **4c** is exactly as expected for an S_N2 process at the alkyl carbon atom.

Cleavage of aromatic methyl ethers by Grignard reagents has been reported but requires drastic conditions.[5,6] Therefore, in analogy to the metalation and halogen–metal exchange reactions,[1a,c] we propose initial coordination to give **7**; this is supported by the observation that THF, being a stronger coordinating solvent than **4a**,[1b] prevents the formation of **7** and, consequently, any further reaction. Activation occurs with the help of a second molecule of diphenylmagnesium by dissociation to the magnesium cation/magnesate complex **8** (Scheme III), which is predisposed to a concerted electrophilic/nucleophilic cleavage of the oxygen–methyl bond. A similar dissociation was indispensable to explain the rotaxane formation between (1,3-xylylene)-18-crown-5 and diphenylmagnesium.[1b] In the absence of kinetic data, which are difficult to obtain because of the heterogeneous nature of the reaction mixture, an intramolecular alternative route via **9** cannot be excluded; however, in **9** both the cationic character of magnesium and the anionic activation of the phenyl group is less obvious than in **8**. We are engaged in a broader investigation including other organomagnesium compounds and alkoxy crown ethers in order to define the scope of this reaction and to support the proposed mechanism.

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(4) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(5) (a) For an overview of aryl methyl ether cleavage reagents see: Larock, R. C. In *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH: New York, 1989; pp 501–504. (b) For an overview of ether cleavage reactions by organomagnesium compounds see: Kharash, M. S.; Reinmuth, O. *Grignard Reagents of Nonmetallic Substances*; Prentice-Hall: New York, 1954; 1013.

(6) The analogous attack of lithium iodide on **4a** requires heating for several hours to 115 °C; remarkably, anisole does not react under these conditions.[3b]